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Ir-2r ALLOYS AS DIFFUSION BARRIERS BETWEEN CU AND SI (100)

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Ir-Zr Alloys As Diffusion Barriers Between Cu and Si(100)

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Various Ir-Zr alloys were studied to determine their effectiveness in high temperature applications as diffusion barriers at a Cu/Si interface. Samples were characterized with XRD, AES, RBS and resistivity measurements. An amorphous Ir_{0.8}Zr alloy was found to be a more effective diffusion barrier than a polycrystalline Ir_{2.5}Zr alloy, indicating that grain boundary diffusion dominates in the Ir_{2.5}Zr film. The films, typically about 3000 Å thick, were found to serve as effective diffusion barriers for temperatures up to about 800°C. The diffusion constants were determined at various temperatures, and the activation energy for Si out-diffusion in Cu/Ir_{0.8}Zr/Si was also obtained.

I. Introduction

Aluminum and its alloys have been widely used as interconnects in integrated circuits. However, Cu has a lower electrical resistivity (1.7 μΩ-cm) than Al (2.65 μΩ-cm), and therefore Cu is potentially a better interconnect material for Si[1,2]. On the other hand, studies have shown that interdiffusion between Cu and Si becomes serious at temperatures beginning at 180-200°C [1,3]. A diffusion barrier at the Cu/Si interface can be used to reduce this interdiffusion. Ta was previously studied as such a barrier, and the Cu-Si interdiffusion temperature was raised to around 300-400°C[1].

Engel-Brewer compounds, involving one transition element from the left and another one from the right of the periodic table, have strong d orbital bonding yielding dense, high melting point metallic alloys[4], and therefore might be expected to serve as effective diffusion barriers. In this work, we chose to study one of the more stable Engel-Brewer compounds, such as Ir₃Zr, to determine their effectiveness as diffusion barriers at the Cu/Si interface. It has been reported that amorphous materials perform better than the polycrystalline [5]; therefore, we will also test amorphous Ir-Zr alloys for this purpose.

Since Ir₃Zr was previously reported to be resistant to air oxidation at high temperatures[6], the vacuum prepared samples were heated in air to mimic a realistic service environment[5]. The samples were exposed to air to determine their stability as well as their effectiveness as diffusion barriers in high temperature

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applications(i.e. in the range 200-500°C). The samples were heated up to 1000°C in air to perform accelerated short term tests of their long term stability in air at lower application temperatures.

II. Experimental Methods

The thin films were prepared by magnetron sputtering. The Ir-Zr films were deposited on a clean Si(100) substrate, while the Cu films were deposited on either clean Si(100) or Ir-Zr/Si(100). The film structures were detected by glancing -angle X-ray diffraction (XRD), and the composition and thickness of the films were monitored by Rutherford Backscattering Spectroscopy(RBS). The deposited films were exposed to air for 2 hrs to examine the effect of a high temperature applications environment. Only Cu/Si was annealed in vacuum(10^{-6} torr) for 30 min in order to compare our Cu diffusion data with published data. The film depth analyses were performed by Auger Electron Spectroscopy(AES) and RBS, and the resistivities of the films were measured by the 4-point probe method.

The AES depth profiles were further treated to remove the effects of the Auger electron escape depth[7], so that the diffusion constants were obtained from these profiles after deconvolution[8]. In our samples, the thicknesses of the Cu and barrier layers were about 2400 and 2700 Å respectively.

In this work, $\text{Ir}_{0.4}\text{Zr}$ (close to Ir_3Zr) and $\text{Ir}_{0.4}\text{Zr}$ were chosen as examples of polycrystalline and amorphous barriers respectively. We will use the prefix, p- and a-, to designate the polycrystalline and amorphous alloys.

III. Results and discussion

1. XRD and resistivity results

Table 1 shows XRD data revealing the extent of copper silicide(such as Cu_3Si and Cu_5Si) and p- Ir_3Zr formation in the Cu/Si, Cu/p- $\text{Ir}_{0.4}\text{Zr}$ /Si and Cu/a- $\text{Ir}_{0.4}\text{Zr}$ /Si samples after heating at various temperatures. Oxide formation was also observed by XRD[9]. After both air exposure and vacuum annealing, copper silicides appeared already at 700°C for Cu/Si. For Cu/p- $\text{Ir}_{0.4}\text{Zr}$ /Si, the copper silicides and p- Ir_3Zr also appeared at 700°C, however, for Cu/a- $\text{Ir}_{0.4}\text{Zr}$ /Si the copper silicides did not appear until around 800°C and became prevalent at 900 and 1000°C. The formation of p- Ir_3Zr formation became significant beyond 800°C. These XRD data already suggest the possible relative advantage of using amorphous materials over polycrystalline. This will be confirmed below.

Fig. 1 shows resistivity measurements for Cu/a- $\text{Ir}_{0.4}\text{Zr}$ /Si heated in air at different temperatures. The resistivity for Cu/Si air exposed at 700°C was found to be much higher than that for Cu/a- $\text{Ir}_{0.4}\text{Zr}$ /Si air exposed at the same temperature. The effect of oxidation is expected to be similar in both cases. Thus the large resistivity difference probably arises from the greater copper silicide formation in the Cu/Si case as already seen in the XRD data. The resistivity of the air exposed Cu/a- $\text{Ir}_{0.4}\text{Zr}$ /Si increases sharply between 800 and 900°C consistent with the stronger formation of copper silicides at these temperatures in agreement with the XRD results.

2. AES, RBS depth profiles and diffusion constants

The AES depth profile for Cu/Si(100) after vacuum annealing at 700°C (Fig. 2), indicates total Cu-Si mixing. Si has reached the surface and Cu has deeply penetrated into the Si substrate. On the other hand, the AES depth profile for Cu/Si air exposed at 700°C (Fig. 2) shows much less diffusion. The diffusion constants for Cu into Si after vacuum and air heating are 2.3×10^{-6} and 4.68×10^{-5} cm²/sec respectively. Obviously, the diffusion is retarded by oxidation which agrees with a previous report that the presence of oxygen in a metal film can significantly retard the growth of silicides[10]. The diffusion constant of Si into Cu after air annealing is 1.35×10^{-14} cm²/sec.

The diffusion constant for Cu into Si annealed in H₂ is calculated to be 2.7×10^{-5} cm²/sec based on the published activation energy and frequency factor[11]. Our experimental result is 2.3×10^{-6} cm²/sec as indicated above; this difference may be caused by slight oxidation in our vacuum annealed sample. A small percent of oxygen (around 6%) in this thin film is indeed indicated by our RBS and AES data.

The AES depth profiles for our Cu/p-Ir₂Si₃Zr/Si sample after air exposure at 700°C are shown in Fig. 3. Si has penetrated through the p-Ir₂Si₃Zr barrier and even across the Cu layer reaching the surface, and oxygen has diffused in through the Ir-Zr barrier. Copper silicides are formed as indicated by the XRD data. The diffusion constant of Si into p-Ir₂Si₃Zr is 2.40×10^{-14} cm²/sec, which is comparable to that in Cu/Si. We conclude, in contrast to that previously reported that p-Ir₂Si₃Zr is not resistant to

oxidation at high temperature, and does not serve as an effective diffusion barrier, probably because of the large grain boundary diffusion in the p-Ir₂Si₃Zr.

The Cu/a-Ir_{0.4}Zr/Si samples were exposed to air at 600, 700, 800, 900 and 1000°C for 2 hr. In the as-deposited Cu/a-Ir_{0.4}Zr/Si films, the Cu and Si interfaces are sharp, and remain sharp after exposure at 600°C for 2 hr in air; however, an increase in the oxygen concentration indicates that this Ir-Zr alloy is also not resistant to oxidation at high temperature. The AES depth profile at 600°C (Fig. 4) reveals no copper silicide formation in agreement with the XRD data, and it also indicates that the a-Ir_{0.4}Zr may still be an effective diffusion barrier at 600°C in an applications atmosphere if the film thickness is only a few hundred Å. The presence of a small amount of p-Ir₃Zr apparently has no effect on the diffusion rate, possibly because only islands of p-Ir₃Zr are formed, which have no grain boundary paths through the barrier. At 700°C, the AES data (Fig. 4) indicate that the Cu and Si are still well separated although the interfaces are less sharp. Still little copper silicide is evident in agreement with the XRD data. The diffusion constant for Si out diffusion at 700°C is 2.41×10^{-15} cm²/sec, which is one order of magnitude smaller than that in Cu/Si at 700°C. However, at 800°C (Fig. 4), the interdiffusion between Cu and Si increases and copper silicides appear. The RBS depth profiles (Fig. 5) support the AES and XRD results. At both 700 and 800°C, the a-Ir-Zr alloys remain in the amorphous state, and any Ir₃Zr crystallites formed are still probably isolated from each

other because of the low volume fraction indicated by the weak diffraction lines. We conclude that an $a\text{-Ir}_{0.4}\text{Zr}$ film with thickness of 2700 Å does serve as a effective diffusion barrier at temperatures up to about 800°C in application atmospheres. The increased effectiveness results from the amorphous micro-structure, and apparent lack of grain boundaries. At 900 and 1000°C, as indicated by the XRD and resistivity data, $p\text{-Ir}_2\text{Zr}$ and copper silicides are extensively formed. Apparently the Ir_2Zr crystallites are no longer isolated from each other, supplying through grain boundary paths which allow faster diffusion. The AES and RBS profiles[9] show strong interdiffusion at these temperatures confirming that the $a\text{-Ir}_{0.4}\text{Zr}$ diffusion barriers are no longer effective at 900°C and above.

Based on the constants for Si out diffusion in $\text{Cu}/a\text{-Ir}_{0.4}\text{Zr}/\text{Si}$ between 600 and 900°C (Table 3), an Arrhenius plot is obtained as shown in Fig. 6. The activation energy (E) and frequency factor (D_0) are 1.93 eV and $1.17 \times 10^{-5} \text{ cm}^2/\text{sec}$ respectively. Our value for E is between the typical values found for interstitial and vacancy diffusion, and D_0 is much smaller than the typical value found for interstitial diffusion. The low D_0 result is in agreement with previous reports indicating that diffusion in amorphous materials may occur via a cooperative process, which is a slow process because of the low probability for correlated atom motions[8,12].

In $\text{Cu}/a\text{-Ir}_{0.4}\text{Zr}/\text{Si}$, chemical complexes involving the infused, such as Cu-O-Ir , Cu-O-Zr , Ir-O-Si , and Zr-O-Si probably form at the interfaces. The bonds in these complexes are not broken at 600°C

and therefore almost no diffusion is observed. Beyond 600°C, such as at 700°C, the thermal energy is enough to break the bonds in these complexes and diffusion occurs. Therefore, a partially oxidized $a\text{-Ir}_{0.4}\text{Zr}$ film can serve as an effective diffusion barrier in an applications environment with thinner layers (a few hundred Å) at temperatures of about 600°C, and thick layers (2700 Å) for temperatures up to 800°C.

In summary, we have found that both $p\text{-Ir}_{2.5}\text{Zr}$ and $a\text{-Ir}_{0.4}\text{Zr}$ are not resistant to oxidation at high temperatures, in contrast to that previously reported. In an applications environment, the $p\text{-Ir}_{2.5}\text{Zr}$ alloy is also not effective as a diffusion barrier at 700°C. On the other hand, a partially oxidized $a\text{-Ir}_{0.4}\text{Zr}$ film (thickness 2700 Å) can serve as an effective diffusion barrier between Cu and Si up to 800°C. A thinner film (a few hundred Å thick) may still work well at about 600°C where the reduced conductivity of the partially oxidized films may not be a significant problem in some electronic device applications. The barrier function in $\text{Cu}/\text{Ir}_{0.4}\text{Zr}/\text{Si}$ may result from oxygen complex formation at the interfaces. The Si outdiffusion is believed to occur via a cooperative mechanism.

Acknowledgments

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Figures captions

- Fig. 1: Surface resistivity for Cu/a- $\text{Ir}_{0.4}\text{Zr}/\text{Si}$.
- Fig. 2: AES depth profiles for Cu/Si heated in vacuum and air at 700°C.
- Fig. 3: AES depth profile for Cu/p- $\text{Ir}_{2.5}\text{Zr}/\text{Si}$ exposed to air at 700°C.
- Fig. 4: AES depth profiles for Cu/a- $\text{Ir}_{0.4}\text{Zr}/\text{Si}$ exposed to air at 600, 700 and 800°C.
- Fig. 5: RBS depth profile for Cu/a- $\text{Ir}_{0.4}\text{Zr}/\text{Si}$ exposed to air at 800°C.
- Fig. 6: Arrhenius plot for diffusion rate of Si into a- $\text{Ir}_{0.4}\text{Zr}$.

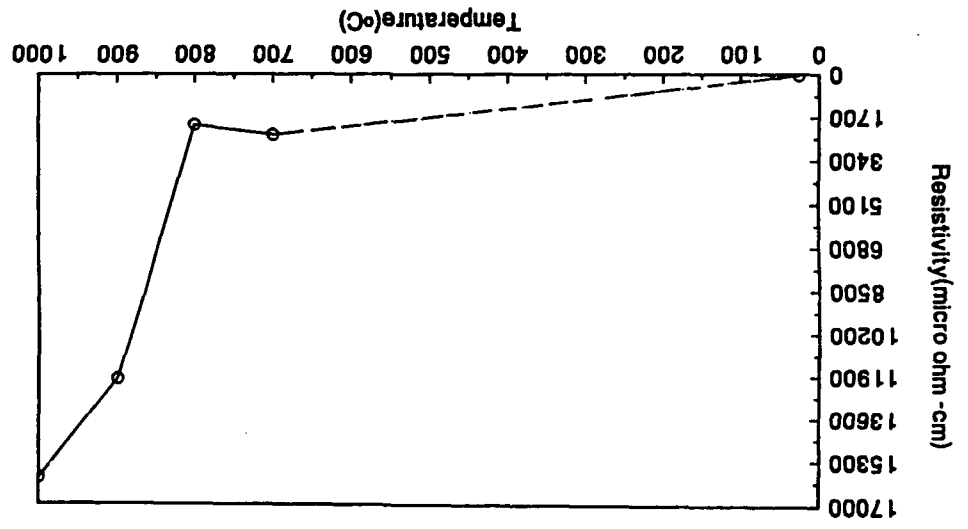
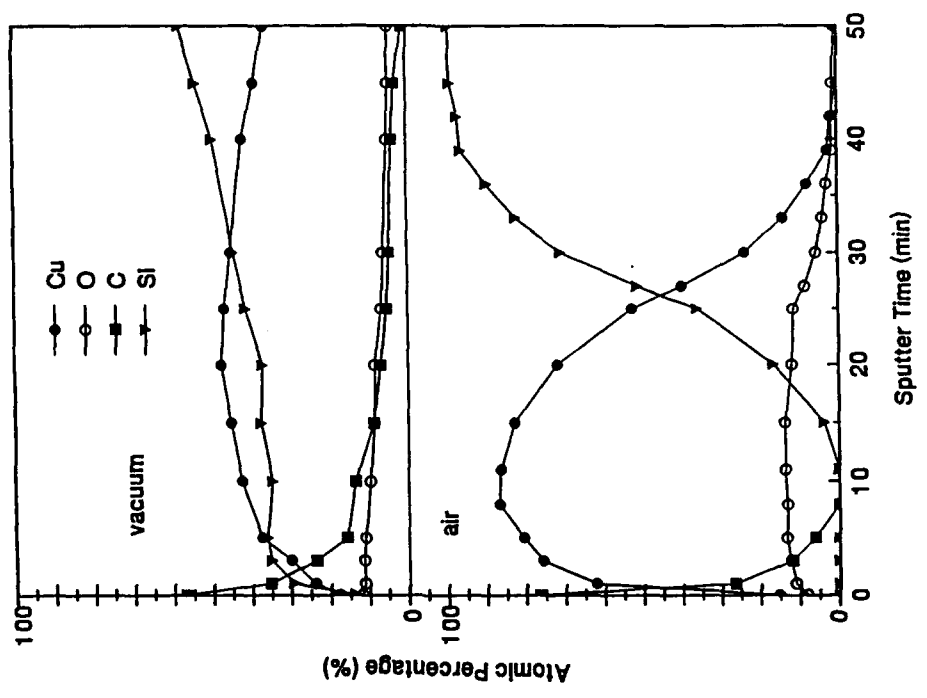
Table 1: XRD data for copper silicides and Ir₃Zr

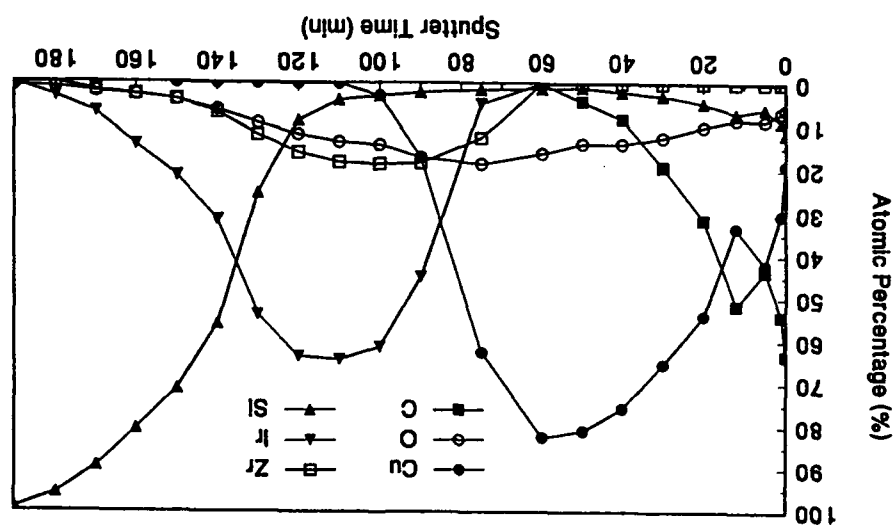
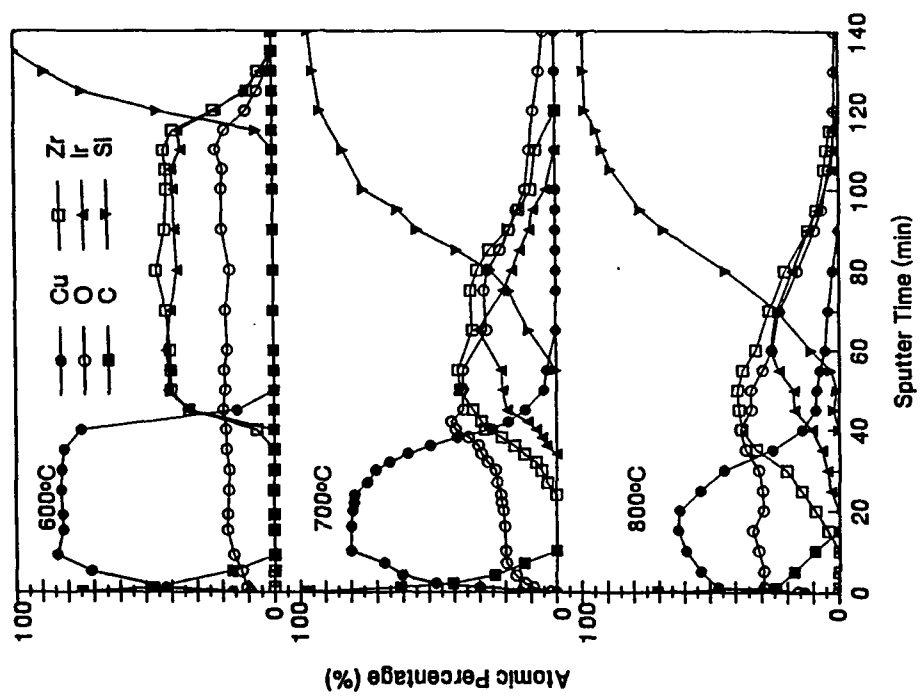
d (Å)	Intensity after annealing in									
	Air									
	Vacuum	Cu/Ir _{0.85} Zr/Si								
	Cu/Si	700 C	600 C	700 C	800 C	900 C	1000 C	700 C	Assignment	
3.26	Cu ₂ Si					M				
2.23	Ir ₃ Zr				M	S	S	S		
2.18	VW					VM		VW		
1.96					VW	M				
1.82		M			M	M		VW		
1.73										Ir ₃ Zr
1.70						M				Cu ₂ Si
1.63						VW				Cu ₂ Si
1.39	VW	M				M			M	Cu ₂ Si
1.37			VW	M	M				M	Ir ₃ Zr
1.19									VW	Ir ₃ Zr
1.15	VW	M			VM	VW		VW		Cu ₂ Si
1.13				VW				VW		Ir ₃ Zr
1.08				VW	VW	VW		VW		Cu ₂ Si
0.99									VM	Ir ₃ Zr
0.90						VW			VM	Ir ₃ Zr
0.87									VM	Ir ₃ Zr
0.80									VW	Ir ₃ Zr

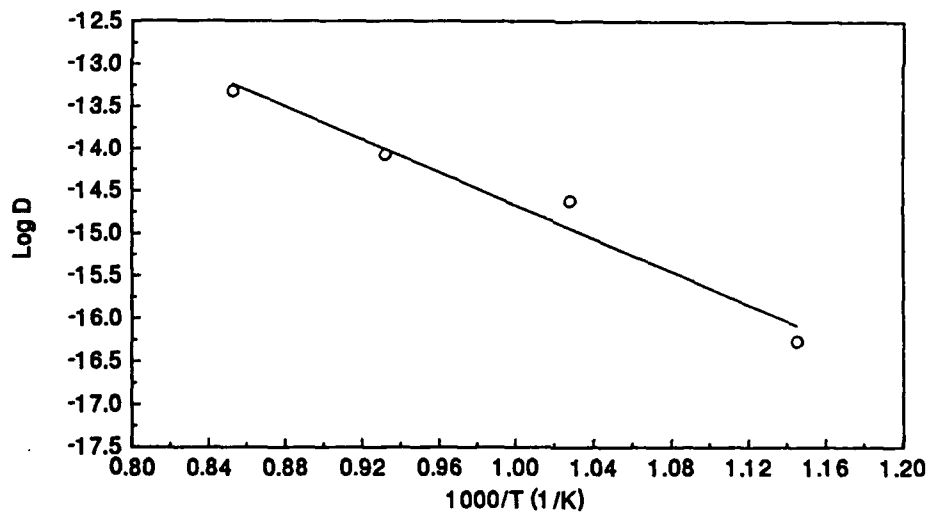
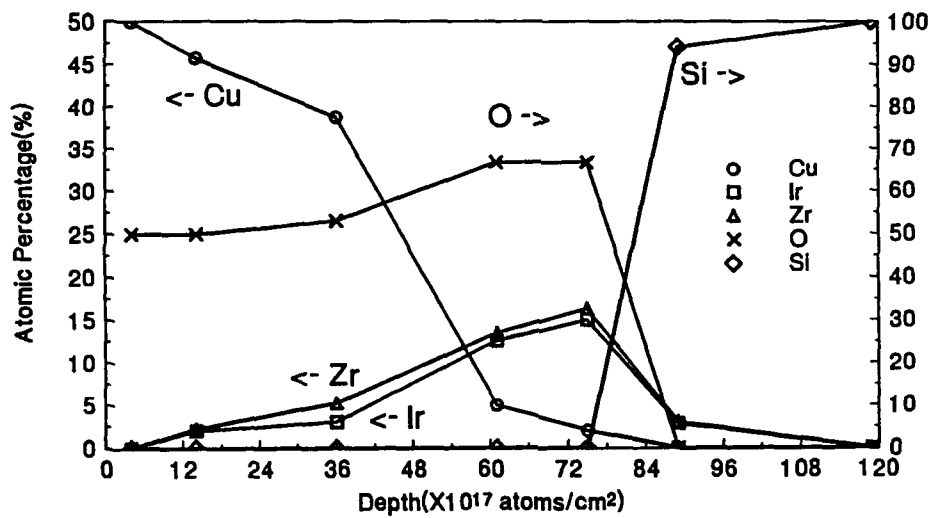
V:very, W:weak, M:medium, S:strong.

Table 2: Diffusion constants

Diffusion	Film material	Temp. (°C)	D (cm ² /s)
Si into Cu	Cu/Si	700	1.35 X 10 ⁻¹⁴
Si into Ir-Zr	Cu/Ir _{0.85} Zr/Si	600	5.40 X 10 ⁻¹⁷
		700	2.41 X 10 ⁻¹⁵
		800	8.44 X 10 ⁻¹⁵
Si into Ir-Zr	Cu/Ir _{0.85} Zr/Si	900	4.76 X 10 ⁻¹⁴
		700	2.40 X 10 ⁻¹⁴







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